

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of

Applicant(s) : Phelps, et al.  
Serial No. : 10/625,915  
Filed : July 23, 2003  
Title : NON-TOXIC CORROSION-PROTECTION CONVERSION  
COATS BASED ON RARE EARTH ELEMENTS  
Docket No. : UVD 0280 IA / UD 268  
Examiner : L. Zheng  
Art Unit : 1742

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

**DECLARATION OF JEFFREY A. STURGILL**

Jeffrey A. Sturgill, one of the applicants in the above-identified patent application, declares as follows:

1. I received a B.S degree in Geology from the University of Toledo in 1986. I was employed by the University of Dayton from November 1993 until September 2006. I have been working the area of corrosion-inhibiting pigments since 1996, and in the area of corrosion/materials degradation since 1985.
2. I am familiar with this application as well as the Office Action mailed February 26, 2007, including the rejections made by the Examiner therein. I am also familiar with the references cited by the Examiner in that Office Action including U.S. Patent Nos. 6,200,672 to Tadokoro (treated as equivalent to WO 98/48075), and 5,322,560 to DePue.
3. I prepared solutions using Tadokoro's process and the organic compounds 2-hydroxynicotinic acid, catechol, dextrose, and salicylic acid. Dextrose was used as a close surrogate to  $\gamma$ -cyclodextrin because  $\gamma$ -cyclodextrin was not readily available.

However, I do not believe that this difference would change the results. Salicylic acid was used because it is slightly less soluble in water than 2-hydroxynicotinic acid.

4. The solutions were prepared as follows. A 1:1 molar ratio of ammonium cerium IV nitrate to the organic was mixed together. Specifically, 0.02 moles of the respective organic was dissolved in 50 ml of deionized water. The organics were catechol (2.2 g used), dextrose (3.6 g used), 2-hydroxynicotinic acid (2.8 g used), and salicylic acid (2.8 g used). In a separate beaker, 10.9 grams of ammonium cerium IV nitrate was dissolved in 30 ml of deionized water. The specific organic was then mixed with the 10.9 g of ammonium cerium IV nitrate dissolved in 30 ml of water.

5. When the catechol solution was slowly added to the ammonium cerium IV nitrate solution, some bubbling occurred at the surface. As the 1:1 molar mixture was reached, the solution gradually became dark and cloudy. Conversely, when the ammonium cerium IV nitrate solution was slowly added to the catechol solution, no bubbling was observed, but the solution also became dark and cloudy as the 1:1 molar ratio was reached. The catechol solution was a tan brown to begin with. The starting color of the ammonium cerium IV nitrate solution was orange. The ending color of the mixed solution was orange-brown once the 1:1 ratio was reached. The solution was an opaque black after mixing for 24 hours.

After the solutions had been mixed for 24 hours, the opaque black solution was filtered. The supernatant was always black (from the extremely small particles formed during the reaction passing through the Catalog No. 28320-085 VWR Brand qualitative filter paper), but enough solids were collected for a compositional analysis. The black solid was analyzed for tetravalent cerium using the procedure described on page 246 of Reagent Chemicals - Specifications and Procedures 10th edition by the ACS Committee on Analytical Reagents, 2006. The analysis was performed by the Quality Control group of GFS Chemicals, which has many years in certifying the characteristics of tetravalent cerium chemicals. Specifically, 2.0 grams of the black solid was weighed to the nearest 0.1 mg. The sample was dissolved in 2 ml of sulfuric acid and titrated with a redox probe. No cerium in either the tetravalent or trivalent oxidation state was found in the

sample. Given the black color of the sample (tetravalent and trivalent cerium compounds are typically white, yellow, or orange in color), and the results of this ACS-approved analysis, it is believed that the solid formed via the Tadokoro et al. procedure is elemental carbon.

6. When the dextrose solution was slowly added to the ammonium cerium IV nitrate solution, some bubbling occurred at the surface. As the 1:1 molar mixture was reached, the solution became dark orange. Conversely, when the ammonium cerium IV nitrate solution was slowly added to the dextrose solution, no bubbling was observed, but the solution also became dark orange as the 1:1 molar ratio was reached. No matter what order the reagents were mixed, the solution, which was dark orange initially, became clear after 5 minutes of mixing. The solution was still clear after 24 hours of mixing, and no precipitate was observed.

The dextrose-containing solution was evaporated down over low heat overnight. In the morning there was only 20 ml of water left in the beaker (from the original 80 ml), and solid material had not appeared. Even assuming the end result was a cerium IV-dextrose complex, the aqueous solubility is so high that it would fall well outside the claimed solubility range. It would not be usable as a pigment material.

7. When the 2-hydroxynicotinic acid was added to the ammonium cerium IV nitrate, not all of the 2-hydroxynicotinic acid dissolved. It was necessary to heat the solution to approximately 60°C in order to get all of the 2-hydroxynicotinic acid into solution. Upon mixing, the solution turned black. A brownish precipitate appeared after 24 hours when the acid was completely dissolved in water (i.e., the bath at approximately 60°C). If the bath was at room temperature (i.e., the acid was not totally dissolved in water), the brownish precipitate started appearing within 5 to 10 minutes, and after 24 hours, the reaction was complete. An analysis was performed on the precipitate formed from the dissolved acid. A copy of the test results for cerium IV is attached hereto as Exhibit A. The summary of the results states TITER - missing EP (endpoint). Accordingly, there is no cerium IV in the sample. The titrimetric curve is also shown. If cerium IV was present, there would have been a noticeable peak. As can be seen, no peak is present.

The sample was also tested for cerium III, and the results indicated that cerium III was present.

The sample which was not analyzed (where the acid was not totally dissolved) will not have cerium IV in it, because the reaction was much more vigorous - i.e., there was much more bubbling. In other words, the undissolved organic was even more of a reducing species than the dissolved organic.

8. When the salicylic acid was added to the ammonium cerium IV nitrate, not all of the salicylic acid dissolved. It was necessary to heat the solution to approximately 60°C in order to get all of the salicylic acid into solution. A brownish precipitate appeared after 24 hours when the acid was completely dissolved in water (i.e., the bath at approximately 60°C). If the bath was at room temperature (i.e., the acid was not totally dissolved in water), the brownish precipitate started appearing within 5 to 10 minutes, and after 24 hours, the reaction was complete. An analysis was performed on the precipitate formed from the dissolved acid. No cerium IV was present. The sample was also tested for cerium III, and the results indicated that cerium III was present.

The sample which was not analyzed (where the acid was not totally dissolved) will not have cerium IV in it, because the reaction was much more vigorous - i.e., there was much more bubbling. In other words, the undissolved organic was even more of a reducing species than the dissolved organic.

9. The reaction involving catechol resulted in a solid. The solid produced was analyzed for cerium content using ACS-specified procedures, and neither tetravalent or trivalent cerium was determined to be in it. This solid is likely elemental carbon. Two other compounds (2-hydroxynicotinic acid and salicylic acid) produced precipitates that contained cerium III. The other compound (dextrose) yielded a highly water-soluble complex that would be unsuitable for use as a pigment due to its affinity for water. None of the reactions produced a cerium IV complex.

10. The process described in Tadokoro is non-enabling for making a tetravalent cerium complex, and it would take undue experimentation to produce a tetravalent cerium complex using Tadokoro's process.

11. I prepared compounds using the process described by DePue at col. 3, lines 23-34. Cerium (III) nitrate, cerium (IV) ammonium nitrate, and cerium (III) sulfate were used as the water soluble metal salts. Sodium molybdate, sodium tungstate, sodium metasilicate, and sodium metavanadate were used as the water-soluble salts of transition metal oxo-complexes. These compounds were reacted at various ratios (75:25, 25:75, and 50:50). The reaction products were filtered, and oven dried for 6 hours. The compounds made are shown in Exhibit B.

12. These compounds were tested for tetravalent cerium according to the procedure described on page 246 of Reagent Chemicals - Specifications and Procedures 10th edition by the ACS Committee on Analytical Reagents, 2006. Specifically 0.5 g of each compound were added to 25 ml of deionized (DI) water, and 3 ml of concentrated sulfuric acid was added to dissolve the material. The solution was further diluted to 75 ml, and titrated with 0.1 N ferrous sulfate in the presence of a redox probe. A copy of the test results is attached as Exhibit C.

13. The cerium molybdates compounds were various shades of yellow. They showed no tetravalent cerium. In the samples that used cerium sulfate, analysis of the solid showed it to be undissolved cerium sulfate (Samples 5 and 6).

14. The cerium tungstate compounds made with ammonium cerium nitrate as a starting material were a faint yellow color; the remaining compounds were white. The analysis showed no tetravalent cerium. In the samples that used cerium sulfate, analysis of the solid showed it to be undissolved cerium sulfate (Samples 11A and 12A). No precipitate formed when 75% ammonium cerium nitrate (Sample 10) was used.

15. The cerium metasilicate compounds were faintly yellow. No supernatant remained on mixing; everything was converted to solid (Samples 11B and 12B). There was evolution of ammonia during mixture when ammonium cerium nitrate was used (Sample 12B). The analysis showed no tetravalent cerium.

16. The cerium metavanadate compounds were vivid yellow. The analysis showed the presence of a strong oxidizer in solid. Using this test method it was not possible to determine whether the oxidizing nature was due to tetravalent cerium or pentavalent vanadium.

17. For the samples formed using ammonium cerium nitrate, washing the samples with DI water after formation of the solid precipitate affected whether the sample exhibited tetravalent cerium using the ferrous sulfate titration. If the solid was titrated as formed, without washing, some tetravalent cerium was observed. However, if the samples were thoroughly washed with DI water (at least one and preferably two or more equal volumes), then the amount of tetravalent cerium observed in the solid was dramatically reduced. These species are water soluble, indicating that they are not tetravalent cerium/molybdate complexes, which would be sparingly soluble. Such high solubility species are not suitable for use as a pigment material.

18. DePue's process is significantly different from descriptions in the literature for preparing tetravalent cerium compounds.

19. On the basis of our testing and the differences between DePue's method and known methods for preparing tetravalent cerium compounds, I believe that DePue's method does not result in the formation of tetravalent cerium compounds.

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The declarant further states that the above statements were made with the knowledge that willful false statements and the like are punishable by fine and/or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of this application or any patent resulting therefrom.

Date: 26 JUN 07

  
Jeffrey A. Sturgill